Tape 1

Ann Mattsson:

All of you, welcome to this workshop on exchange-correlation functionals in density functional theory. Density functional theory, or DFT, was founded in 1964 when Kohn and Hohenberg formulated the Hohenberg-Kohn theorem. In 1965 Kohn and Sham used this theory in turn to formulate the Kohn-Sham equations and that's where the exchange-correlation functional showed up for the first time. In this same paper, Kohn and Sham gave the first approximation for the exchange-correlation functional, the local density approximation or LDA. The LDA was the cornerstone of density functional theory and was the only functional used, then mostly in physics, up until 1986 when John Perdew and collaborators constructed the first general gradient approximation or GGA. With GGA, DFT found its way into chemistry and in 1998 this resulted in Walter Kohn, and he's sitting over there, being awarded the Nobel Prize in chemistry. DFT is today an indispensable tool for understanding materials worldwide and also at Sandia.

Today at this workshop we have both chemists and physicists and also some who do not know if they are chemists or physicists. I must say I'm very proud to be at the center at Sandia which is named Physical and Chemical Sciences. So not only do we have both physicists and chemists here today, we also have people both using density functional theory and developing it. Development of density functional theory at Sandia has long been focusing on expanding capabilities and today we are at the situation where the limit on density functional theory is more due to the approximate functional than on the computational capabilities. If it can be stated we are in some cases very accurately calculating the wrong number. And that is why we are here today, to investigate the facts about functionals available today and investigate strategies for better functionals.

As I said we have both chemists and physicists here today, users and developers, students and emeritus professors. What is the reason for me to bring such diverse people together? I strongly believe that new science or breakthroughs are created at the intersection of different fields and that an old fact in a new context can make all the difference. So let me last give you all these words by Marcel Proust in this motto:

"The real voyage of discovery consists not in seeking new landscapes, but having new eyes."

We should all think about that during this workshop. So with that I give the mike to John Aidun who will be a stand-in for Bill Camp, who couldn't come, but he will give a short overview of the center CSRI.

Good afternoon, I am John Aidun, Manager of the Computational Materials and Molecular Biology Department, and in my department we both develop DFT code capability and apply it to do our work. I'm here today to welcome you on behalf of David Womble, who is the director of the Computational Sciences Research Institute, in David's absence on business travel. And I'm standing in for my and David's boss, Bill Camp,

who's director of the Computations Computers Information and Mathematics Center. Bill was looking forward to doing these honors and regrets he couldn't be here, but he was detained by strenuous negotiations he's in the midst of with Cray Computer Company negotiating the design and acquisition of the next generation massively parallel ASCI computer known as Red Storm.

I'd like to take a few minutes to give you an overview of the CSRI, to introduce you to opportunities for collaborative research that it provides. The Computer Science Research Institute is an enabler of new science through advances in computation. It does research in computer science, computational science and mathematics. This is done specifically and exclusively through collaboration of university faculty and students with Sandia staff, and this is done to achieve mission critical success for the national laboratories and the Department of Energy. Opportunities include sabbaticals and summer faculty positions, post docs and summer student positions, graduate fellowships, the institute sponsored workshops such as this, for which it is a co-sponsor, and technical visits and colloquiums. There's a wide range of technical areas that are of interest at the CSRI, many of them have to do with enabling PDE-based methods, computational methods for solving PDEs including meshing as preprocessing for your finite element simulation and visualization of your results. I want to call your attention to a recent addition, multi-scale modeling, which includes multi-scale material modeling for which quantum methods and DFT, in particular, provides the underpinnings. This current fiscal year has been a very active one for CSRI; it has participated in 13 long-term projects, 81 short-term visitors, many summer visitors, students and faculty and sabbaticals. It sponsors, or actually has, five fellows who come through the High Performance Computational Science Program out of DOE and the National Physical Sciences Consortium. It hosted several workshops, five this year, and supported four others and has an active and ongoing seminar series. More information can be found on Sandia's open site at cs.sandia.gov and again David Womble, the Director, dewomble@sandia.gov.

And with that it is my pleasure to introduce the two Sandia Vice Presidents who have particular interest in this workshop and its outcome. Both of these gentlemen place a high value on science and technology as a critical component for achieving Sandia's missions though they come at it from slightly different perspectives. On the one hand there is DFT as promoting basic science and technology capability, which is important for our technical staff's work and on the other hand, DFT is looked to both as a driver for development and computational science and also as requiring considerable computer capability and computer capacity. So next we'll hear from Al Romig, who's the Vice President for Science and Technology, and he'll be followed by Tom Hunter, the Vice President for Information, Computation and Engineering Sciences.

Al Romig:

Thank you John.

First off, on behalf of the laboratory, I'd like to welcome all of you who are visitors to Albuquerque and to being in the shadows of Sandia. I was very personally excited about

this workshop when I first heard that it was going to happen several months ago. It's interesting we live in a world right now where there are so many large meetings that are sponsored by large professional societies and the like, and even people that have figured out there're ways to make money by having meetings who go off and run them, that having something that is really as focused and collegial as this one is really something quite special. Really a way, I think, to get at some really basic fundamental problems that we can all work on and grapple with and share our ideas together. So I really think that these kinds of things are wonderful ways to progress the state of the art. I'd also like to thank some very special guests that we have who have taken time out of their schedules to come and participate with us over the next couple of days. Walter Kohn and John Perdew and Michael Teter, we thank you all to our visitors for coming and spending some time with us.

Most of you probably know something about what the mission of Sandia is. It's about national security in a number of different regards and I suspect Tom will say a bit more about that, but if you look at how this laboratory meets its national security mission it does it with an underpinning of science and technology and we have very major investments in materials and process sciences, microelectronics and microsystems, advanced computation, engineering sciences, high energy density physics and the basic physics and chemistry and nanotechnology that underpin all of those things. Depending on how you count the dollars, the total amount of investment here that would look like, let me just say use the term that the DOD does, 6.1 and 6.2 basic and applied research, we spend about $350 million a year at this laboratory in things that fit that basic definition across those areas that I just described. And I think one of the very special things about the laboratory is how those technologies can integrate together with one another.

One that we're particularly excited about right now is a new project called MESA, which I like to describe as computationally enabled Microsystems which really blends nanotechnology and microtechnologies for micromachines to microoptical devices, etc., and trying to realize product out of that using computational tools in a way that has never been done before. Sandia in partnership with Los Alamos has just been fortunate enough to be awarded one of the nanotechnology centers up at the Office of Science, called the Center for Integrated Nanotechnologies, which we think will build a wonderful base tapping into the computational skills and the microfabrication skills at these two laboratories to allow us to move forward in more fundamental issues around nanoscience. Also some very major investments, as I said, in high energy density physics and one of the spin-offs that comes into here from our so called Z machine is the ability to begin looking at a very novel high pressure equation of states of matters and beginning to look at matter under conditions that are very unique and very different than those we've been able to explore before. A lot of our work so far has been computational, but we've worked with our colleagues at the other two laboratories, Los Alamos and Lawrence Livermore, to try to understand those theoretical underpinnings and know that there is a lot more to do from the computational basis to sort of pursue that. If you look at the actual function of this workshop, as I said, we really thought that getting people together, in the sense of the area that you all represent, would be a real opportunity to have some cross fertilization to solve problems and discuss things in a way that we don't normally

have access to. So I would encourage you to maintain that open and discussive atmosphere while you're here in order to achieve that goal.

It's actually fairly interesting to understand, I think, how this whole thing fits into the larger picture and I'll even share with you a personal war story about how I wish that we had this state of the art in computation back in the days I had a real job, had to do things, so to speak. I was one of those people and a few of you know me and are old enough to remember this. I did a lot of what was called modeling at the time when modeling wasn't a very common word because the experimentalist thought I was a theoretician and the theoretician thought I was an experimentalist. I had them both fooled. Worked just great. But if you look at what we've been trying for decades now here at this laboratory, trying to understand how things work at the system level and try to find ways to create new materials, new processes and new devices and understand their behavior using modeling and simulation to do that. In the days when I did this thing, we didn't really know how to do this sort of work in the early 1980s, at times we were in the position of trying to use rather empirical methods to get at some of the real routes of things. In fact I remember a problem that we had in the mid 1980s involving something called […] in integrated circuits that shut down the production line. We had a problem [...] and when they came off the shelf to go into a system […] work more. And what we eventually found was that it was a nation of stress and basically a stress driven diffusive model or mechanism that was called atomic migration diffusion that was causing open circuits in this. As we tried to model that diffusion process, we found ourselves in the need, which is really kind of in this sort of dimensional scale, we found ourselves in the need of some very big transport diffusion coefficients to solve that problem. And there was no time to do that nor did I want to fool around with radioactive tracer elements at the time and so we ended up using embedded atom methods, which are rather empirical, to extract those numbers and there is a lot of uncertainty with those kinds of empirical numbers, but we managed to work our way through a process to get to the answer. But if I had been able at the time to use these kinds of tools to get a handle on some of those fundamental numbers it would have had a major impact on trying to solve a problem of real importance to the laboratory at the time.

In fact now we can look at a lot of issues in the laboratory involving materials, trying to understand how they behave, where this kind of modeling is now having a real impact on actual national security issues, products, etc., that are important to us here at the laboratory. So it's exciting to see the work have advanced to the point where it's able to solve real problems number one, […] , the kind of excitement that will attract bright new young talent into the laboratory. So from the most forward looking perspective of talent and good work at the laboratory, this sort of thing is critical to us as is the fact that we're now at the point we're now able to begin to do things based on these kinds of analysis have a real impact on things that are important to the laboratory in its mission space.

I'll close by thanking all the organizers, John and Charles Barbour, and especially Ann Mattsson for all the work that you've gone through to make this happen. I think many of us have had nice things and know how much work and pain it is to do that. Somebody had to step forward and do it and Ann was the person who did it for this one so I think we

all owe her a round of applause for her efforts to do this. Once again we're delighted to have such an esteemed august group here with us for the next few days to discuss this important issue and I hope you enjoy your next couple of days.

John Aidun:

Next Tom Hunter the Vice President for Information, Computation and Engineering Science.

Tom Hunter:

Let me add my welcome to Al's to this workshop. It's a real opportunity to bring people together to address this very important topic. I can share the dilemma of not knowing whether one is a chemist or a physicist, my training is in nuclear engineering and material science and if you don't know nuclear engineering, it's a field where you're accepted neither by the engineers or the physicists as a real profession, but we just did quantum mechanics.

I want to comment from two perspectives on this workshop and it really goes along with the two roles that I have for our laboratory. One role is the head of the nuclear weapon program at Sandia, which is responsible for those elements supporting the nuclear weapons mission we have from research through production, and the other is, as we've heard, about my role as a steward for advanced computing, advanced scientific computing, especially at Sandia. And I share with you a bit of what Al eluded to is that as we look at our laboratory, we have found that we are addressing a very important and significant challenge issued by the nation, and that challenge is that we will always make sure that our nuclear weapons, which represent our deterrents, are safe, secure and reliable and more important that we have to certify to that. We have to actually sign our names saying that is true and that's a very awesome and significant responsibility for all of our laboratory, but particularly for those, Al and I and our lab directors, that have actually put our names beside that statement. So because of that we feel like we must invest in understanding both at a fundamental level and an applications level and since we feel so strongly about truly understanding things that many times can't be evaluated, tested or completely understood, we're going to do everything we can to invest in expertise and judgment to allow us to make predictions and to help our understandings.

Further we want to be leaders in the evolution of engineering in this country. Engineering is evolving to an era in which we no longer do all the complicated testing and all the empirical evaluations that are done historically, but in fact we rely heavily on advanced computing and modeling simulations. You just heard that Bill Camp, who would have been here, is off negotiating an agreement hopefully with a computer supplier to provide us a computer in the range of 20 to 40 tera-operations per second, which in fact will enable us to even better live out that goal of leading in revolutionary engineering. And the ability to predict things which are not totally understood is a commitment that requires us investing people in modeling and simulation. You probably recall, I don't know whether it's Casey Stingle or Yogi Berra, who said that predicting is

hard, especially about the future. Well simulation is very hard, especially when it deals with a reality and we have to address that question straightforwardly. There is a lot of predictive modeling that's important to us. We worry about a lot of things like how do things age. Al mentioned the stress boarding issue in microcircuits; well that's an important question. We also worry about absorption, materials in desiccants, about chemical reactions and their influence on corrosion. We worry about response to adverse environments, we worry about radiation effects all the way from global things down to single when upsets in silicon and integrated circuits, and then we worry about very small devices. If you think about what characterizes Sandia's largest investment in the future, it's about small smart things. Small smart things don't always limit themselves to macroscopic understandings, so we have to worry about how small little machines work, in particular, how integrated systems work which combine optical systems and chemical sensors and processors and little machines all together. So we care about that and we intend to invest in that and underlying all of these things there is a hierarchy of scales and hierarchy of phenomena that push both physics and simulation. And at the core of that is an underpinning of quantum mechanics, which you're going to focus on today.

Let me switch roles and talk about my advocacy in stewardship for computing. We believe and are committed to the transforming power of computing in science and engineering. It truly will define, I think, where this century is going to go and certainly the first couple of decades will lead us in that direction. We're going to deploy a lot of simulations in complex phenomena which go beyond our experience base and our ability to test--very important. We'll be predicting things that we can neither test nor observe directly and, as we get further and further out on that limb, we have to be sure that our simulations are grounded in some solid science; again this judgment coming back to reinforce what we conclude. And in many cases that core, that thing, which gives us the confidence that we can make predictions and certifications in those predictions, is going to rely on such things as density functional theory and we've got to build that core and this effort, as this workshop atests, is to build that core. As you heard from John, computing itself needs to be relevant, it needs to deal with tough problems, it needs to deal with things which challenge the minds of those developing simulations and challenges those who can provide information which can be put into a computing framework. And so because we want to challenge the computing frontier, we want to pursue these areas: the areas of trying to understand how in fact we can better go to the very smallest of atomic scales and understand what might be happening. So we have commitments that we have made of investments that match that, we have work for workshops like this and now the challenge is to explore what knowledge we have and ask how it can really open up new frontiers for us and better understanding of materials and their interactions. And I really think this is exciting, I think it's a rare opportunity for us to get together and to think about things which we don't normally fill our day: Al and I spend our days on a lot of other topics, but this is very exciting. We're glad to lend our support and glad you could all be with us and we thank our distinguished guests for being here and look forward to the next couple of days. Thank you.

Walter Kohn:

I'm very happy to be here at this meeting. Having listened to two vice presidents who have just preceded me, I noticed that the words understanding came up many times and I'm very happy about that. Particularly I'm impressed by the fact that an institution like this laboratory, which has extremely important applied responsibilities, nevertheless there's an appreciation for the importance of understanding. I liked Ann's quotation of Proust very well. I would like to mention something that I was told by a great scientist which is along the same line, a little more specific. The great scientist was Eugene Wigner. When I was teaching at Carnegie Tech in Pittsburgh, he once came through to look over the department and talk to people, including the very junior members, and we talked about various things. And I really don't remember the subject, but I do remember one instance about the subject. I explained something to him and it seemed a little strange and he said, "Did you get that same conclusion in some other way?" And I said "No, but I'm sure this is right." And he said, "You can't really be sure something is right unless you understand it in at least two totally different ways." And that has been a very useful motto for me; pass it on. And it's related to Ann's, a look at the same thing, but with new eyes. Here we are.

We have in this room a number of people that really made a great part of density functional theory into what it is today. And as I look around, I realize each of them have different scientific personalities and quite different perspective and I think that's the great thing about this field is it's not being a kind of one-dimensional effort, it's been a complex multi-dimensional effort. A little historical correction: that quote attributed to Yogi Berra…actually, I heard it more than half a century ago and it was attributed to an equally renowned person, Niels Bohr.

I have to confess, I prepared these remarks on the plane here, and I thought this would be actually a good idea to play it loose and see what's here and what the atmosphere is and so on. So I'm going to write down very few words on this transparency just to guide our thinking. Somebody suggested that since I got up at 4:30 this morning and having counted on having a little nap here, but arriving 5 min. after lunch had started, so thought there was a danger that I might fall asleep at my own lecture, not to speak of the danger of the audience falling asleep. After lunch, you know, all these negative circumstances. There is a recorded case of a lecturer falling asleep at his own lecture and I'll quickly recount that. That was a very fine scientist, Placzek, one of these early theoretical physicist/chemists. He was at the Institute of Advanced Study at Princeton during the time that Oppenheimer was the director. So he gave a seminar and, like all seminars that Oppenheimer attended, he was immediately interrupted and had a hard time, really, saying what he was trying to say. So eventually he said to Oppenheimer, "Why don't you come up to the board and explain what you're trying to ask about." And so Oppenheimer came to the board and he got more and more involved in what he was trying to say. In the meantime Placzek was sitting there and fell asleep and then Oppenheimer had to wake him up. So I hope somebody's ready here.

I think that's a useful thing to do. I've mentioned the fact that we all have different perspectives and in this business I have, perhaps, the longest perspective. And so I thought I would, from today's standpoint but with a historical perspective at the same

time, give one way of looking at where the density functional theory is today and, in particular, where this quest for exchange correlation functionals is. This is like looking for the dodo or some other mystical beast. I'll say a few words about that.

In density functional theory we have a kind of a major shift of perspective from wave functions (everybody here isn't a vice president for technology or knows quantum mechanics…there's a wave function, we're dealing with many particles), to electronic density (to a function of one three-dimensional variable). So it's a quite different way of going at physics, chemistry, material science, plasma science, anything that involves atoms or their constituents in interaction with each other. So this is wave mechanics and this is density functional theory. Here, let's say if you're dealing with a material system, if you really think this way, and you write down the Schroedinger Equation, the partial differential equation in, let's say, 10^{22} variables. So it's something that obviously is always mystically valued, no real value. Electron density distribution is something that one can and does, of course, work with. And my own intention was really directed that way from reading the metallurgy literature, where charge density distribution now is a very important concept. And so I was pushing this along and eventually asked the question: the density has taught metallurgists a great deal, it is, in fact, the whole information in there if you know how to get it out. So then, as Ann mentioned briefly, there was the work of Hohenberg and myself. And we established a kind of existing theorem that said that this really is a possible quest to do everything in terms of the density rather than the many-body wave function. So we had an existence theory, the language was rather a mathematical language in that first paper talking about this shift.

Of course, everything has precursors and I'll mention two important precursors to modern density functional theory. One was the so-called Thomas-Fermi Theory. And what it shared with density functional theory was the emphasis on the density. It was a heuristic theory; it did not have any solid basis. And it made assumptions of smoothness, that the density was a very smooth distribution, which one knew in real material systems was not really satisfied. And so one was not surprised that for applications, particularly in material science, it was not useful. It gave no chemical binding whatsoever. Nevertheless it was already a very brilliant conceptual advance. So that's more or less the level of this first paper.

 And then the other paper that Ann mentioned was by myself and Sham and so this is math [the previous paper]. Now then, the second level was "reality-assisted" math. That was the second paper in this development by Lou Sham, now for many years already a faculty member at University of California, San Diego, and myself. We took this rather formal theorem and used the fact known to me that there had been another approximation, another predecessor. I mentioned Thomas-Fermi, who's predecessor (A), perhaps, and here I mention predecessor (B), Hartree and also Hartree-Fock. In the Hartree equation also the density plays a very important role. The Hartree equation can be looked at in many different ways, a mean-field equation, as a kind of early stage of a modified density functional theory. You look at it and learn all kinds of things. What we learned from the Hartree equation was that the kinetic energy, which is treated in a very crude way here, in fact that such a crude treatment of the kinetic energy was hopeless if

one wanted to get quantitative results for real physical and chemical systems. So we learned that kinetic energy and you know there's all these problems, they are really deep problems. So Hartree's work was done in the 1920s and this study of kinetic energy goes on today, intensively, and will go on in the future. It is long-range research, but fortunately on the way it has yielded quite a lot of results. We had these Kohn-Sham equations and, as Ann said, this is where for the first time the specific subject of this conference came up, the exchange correlation functional; it's a number, an energy, that is determined by the charge density distribution of the electrons. And there's related objects which came by functional differentiation of this, which is the exchange correlation potential, r-dependent potential, but in addition depends also on the entire density distribution, functional of r and a functional of the density distribution. So this appeared, these symbols and these concepts appeared close to 40 years ago now and an enormous amount of very good science have been done to penetrate the meaning of these things and look at them not from one or from two angles but from very many angles and it's been very productive. This is why density functional theory is now both in solid state physics and chemistry, in material science. Certainly whenever you talk about systems consisting of more than a handful of atoms, it's the method of choice.

These were concepts. We made the first rather obvious approximation to this; it was a local density approximation, in that paper. (I didn't realize we'll need more than one transparency.) And the local density approximation used, really, a concept that is already present in Thomas-Fermi theory, but applied to a new object, namely, to this exchange correlation functional. The concept in Thomas-Fermi theory was that they applied it to the kinetic energy, that there's a kinetic energy, which can be thought of as being composed of independent contributions from each volume element. And we used that way of thinking and applied it to exchange correlation functional and that led to the so-called local density approximation. So we talked about mathematics and reality-assisted mathematics; writing down the Kohn-Sham equations, already we used the fact that the kinetic energy needed to be treated better, radically better, than in Thomas-Fermi's theory, that the mean-field idea of Hartree was a big part of the story, but not everything and that then our task was to deal with these objects. That's the subject of this conference and that is where we got now involved with physics and chemistry.

I start with physics. These functionals that embody the really complex many-body aspects of systems of many atoms, to understand them and to put them into forms that are usable, can be used in simulation, always need the understanding as an underpinning for the simulations. This is where physics came in and several of the chief practitioners are here and they have contributed now over several decades to a deeper understanding and better practical forms for this exchange and correlation energy. The physicists tend to work from basic principles, sum rules, scaling laws, asymptotic behavior. A basic principle that, I think, had been very well intuitively understood for a very long time by both physicists and chemists is something that I introduced about six or eight years ago. [To do enough in the …. By the way, it is about a local part of a large system, large in the sense of … and you're looking at a local… and, (Walter Kohn is talking about "nearsightedness" here)] putting this loosely, but just to convey a sense it does not depend on things that are very far away.   It is a little bit on the one hand common sense,

on the other hand very surprising because this wave function flows all over the place and why is it that this local property doesn't "see" what's happening far away? That for me has been a helpful perspective and for other people also. Linear scaling was always an important physics concept and one of the main personalities in this business is here, Dr. Yang.

So physicists contributed a great deal here, a very important role going beyond the LDA, which introduces the gradient of the density. That turned out to be enormously fruitful and improve the accuracy of the results of density functional theory by something approximating, an order of magnitude. And that turned out to be decisive for chemistry, particularly, because it's now brought the accuracy into the so-called range of chemically required accuracy.

So physicists brought a lot to the table here but chemists did also and in a different style. Of course, we already have remarks here that some of us are somewhat schizophrenic and don't know really where we belong. Nevertheless we all know that there is some difference between a physics style and a chemistry style, a very key [person] who contributed to this more chemically perspective has been somebody who in fact was trained as a physicist, I believe, namely Axel Becke. And there with chemists who find part of the tradition, part of the history going back to the periodic table, you look at groups of atoms, you look at regularities when you compare series of atoms and you look at classes of systems rather than looking deeply into a particular system, you can learn something on classes. You introduce with much less hesitation than physicists some phenomenological parameters and then look at measurements to fix them. It was a different game and these contributions there have been often very mutually reactively by physicists and chemists, have basically brought us to this place today where density functional theory is a practically very useful approach.

I want to bring in another kind of perspective here. One of the, I think, very attractive aspects of the local density approximation is that it is completely parameter free; it is electronic structure of anything and has not a single parameter. Parameter free, that's great. In fact physicists feel it's wonderful, no parameter. Of course, it isn't very accurate and that's the price you pay, this balancing business, and I started really working with Ann to add to this viewpoint of universality. The gradient development also strive for universality and they've been very successful, but there is another more chemical viewpoint that says, you have this one approximation, LDA, and you use it for systems that are chemically or physically totally different. You ignore the fact that you know that they're totally different, that for this kind of system that's a good metal, you have a different organization of the electrons than for an insulator with a big energy gap. And why do you ignore this, you know that you should perhaps think about them differently. I had a very excellent disagreement with Roald Hoffman at Cornell, when I gave some lectures there, who started out saying you know, yes, I see you get all these good results, with the LDA, for example, but you don't really get any chemical insight so I don't like it. So I was there for three weeks and he began to publish papers with density functional theory. Actually his students did it because his students found it just too useful not to use and then he had to kind of fall in behind his students. I want to put here physics and

chemistry and then another universality like the LDAs or the gradient approximation versus particularity and I think having both points of view in mind is productive.

Then my last remark, very brief, is so this Holy Grail. People who really haven't thought seriously about the subject, I'm sure many people have had the same experience; they'll come and say do you think that the exact exchange correlation functional will ever be discovered. Now those of us who are struggling with it know this is not a good question, but let me ask a different question, which I think is a reasonable question: What are the ultimate limits of density functional theory? Are there such limits or can we expect that, like most things in science, it gets better and better and where are their limits? I happen to think there are limits and I think we're not terribly far from them but we have a way to go. I would say something like one order of magnitude in accuracy after which I think we'll effectively reach limits. And in conversational discussion I can expand on this, but I won't do it now, but that is something we should kind of keep in mind as we are progressing in this workshop. Thank you for your attention.

Ann:

[(Not transcribed, organization of the workshop)]

I want to introduce Mike Teter, who is chairman of the first session, the applied session.

Mike Teter

I'd like to talk to you today about current problems and opportunities in DFT from a very narrow-minded viewpoint, namely my own. And if I forget the breakthroughs that any of you have thought of, you're free to hit me over the head with them, but I'm going to talk to you about one man's journey into DFT. I started all this stuff when, working for Corning, I decided that we were trying to overcome 200 years of materials ignorance and stop doing the same arguments over and over again by seeing if we could get a good model of glass chemistry. I heard that it was possible using this new thing that Walter had invented to simulate materials with unprecedented accuracy and simplicity so I went off to study with a guy named John Joanopolous at MIT and I became his oldest post doc in the history of MIT. And after being given a foot and a half of reprints, he thought he'd seen the last of me. When I actually showed up six weeks later and asked questions about them he hung his head in shame and decided that he'd have to get me to do something useful or else have me killed. There are many who think he did the wrong thing.

I'd like to talk to you today about DFT not from as wise a position as Walter Kohn, but as somebody who has tried to struggle through understanding this through more than one way and, to borrow something from the spaghetti westerns, we start with the good--just simple LDA results in molecular geometries and vibrations on a par with those from [lower plus ???] and Moller-Plessett second order perturbation theory, significantly better than Hartree-Fock. And the big errors in LDAs are total energy errors, but the great incorrections lower these energy areas by nearly an order of magnitude. So this is the good. Now the good is a little puzzling because LDA is a simple model and the question

is why are these geometries so good, why are these vibrations so good? Many answers have been given over the years, but I'll give you one man's history of this.

We were puzzling over this problem and out of sheer perversity I started doing some many-body calculations on light molecules. And I was a fan before this of the density matrix approach rather than just density functional theory, so I started studying the two-particle density matrix and the exchange correlation holes. And as you went up the ladder from single-determinant Hartree-Fock to single excitations, double excitations, triple excitations and quads, what you found was the exchange correlation hole basically localized and followed the electron around. And if you look at what LDA does, it assumes the exchange correlation hole of the homogeneous electron gas, which is localized, and follows the electron around. So the first thing that you were building into the theory was a rather good model of the way that a correlated electron behaves.   And I may or may not be right, but I accepted this as the reason that you got better than Hartree-Fock results because in Hartree-Fock the exchange hole can be as large as the entire molecule.

The bad. The bad list is a little longer. The first thing is that gradient corrections to LDA do not give uniformly better geometry and vibrations than LDA. Now this is rather puzzling because, if the total energy is an order of magnitude better than LDA, roughly, and it is constrained to stay so, one would think that its changes would also be roughly an order of magnitude or better, but they're not.

Number two: LDA both with and without gradient corrections has a significant electron self-interaction. If you look at simple LDA it disappears exponentially; as you get far from an atom, there's no $1/r$ potential pulling an electron back in making things like negative ions unstable out in space and other strange and wonderful things. Now this disturbed me greatly because, simple-mindedly, I knew oxide glasses have an O double minus ion in it and, if negative ions weren't stable, how could I model this? Of course, I was too stupid to realize that they're counter-balanced locally with positive charges so you didn't have to worry about this, but I spent a great deal of time worrying originally about negative ions and things.

The self-interaction correction of Perdew and Zunger, and throughout this talk and the conference in general you're going to keep hearing the name of John Perdew, who has been extremely seminal if slightly misguided throughout this entire field, but as a pioneer in nearly every advance that happened, he's taken part. There's a recent improvement to Perdew-Zunger by Lundin and Eriksson, but it still has the same problem with different operators for different states. Finally when I was trying to do a simple improvement, not based on gradient correction, but an integral weighted density thing, what we found is that we could improve the heck out of energies just like the gradient corrections for the very simple weighted density model, but you had to do things like core partitioning to get the agreements to agree with real chemistry. And we traced this down to basically treating all density the same; that electrons really want to exchange not only with nearby electrons, but electrons of the same energy. Let's take the lithium diatomic molecule, instead of say this exchange correlation hole is of all the density, you say you're treating a

valence electron so it only exchanges with the valence density and the core is only exchanged with the cores. And that gave much better [results] and, indeed, carried to the ultimate limit, it goes back to the correction of Perdew and Zunger, that's partitioning with a vengeance, treating every state as its own partition.

We looked and published a paper on the improvements in lattice constants and physical properties as you went to generalized gradient corrections. And the results were mixed, and they had to be mixed, because in many cases LDA gives almost exactly the right results, but we were able to trace these down into the following problems: incorrect geometries come from incorrect forces on the nuclei, the forces on the nuclei come only from other nuclei and the electron density. The other nuclei locations you know exactly so you have to have incorrect electron density to give the wrong forces. And if you have the incorrect electron density, that has to come from an incorrect electron potential. So the biggest problem that we could see with generalized gradient corrections is that they did not improve the potential acting on the electrons. So a natural question here was, what's the right potential. So we again started doing some many-body calculations and trying to derive the correct potentials and that's a story I'll go into a little later, but it's not that much fun. A full configuration interaction calculation was performed with large basis sets and light molecules. The exact electron density can be derived, not without difficulty; the Kohn-Sham potentials causing these densities can be obtained. We've done this and our model calculations, the lithium diatomic molecule, for several reasons: number one, with only 6 electrons you can treat it with very highly correlated level, you certainly don't have to worry about relativity, you can actually afford the kind of basis sets that you need. H_2 is even better, but somehow we didn't feel that was interesting enough and it's clear that the potentials that you get from these studies differ significantly from those derived from the best gradient corrected results. It's the electron density differences coming from these potential differences, which causes error and forces errors in molecular geometry.

Just a word about the calculation: Hartree-Fock densities, LDA densities differ from the exact densities by only a few percent; they're actually pretty close. If you want to really well-characterize the density differences, you have to do calculations down at a tenth of a percent in density. But as Walter has taught us, the problem is variational in density, so if you do calculations to a tenth of a percent in density you have to resolve the energy to a part per million. How many chemical basis set do you know that give you micro-Hartree results? Not too many; so the first thing you have to do in all this stuff is invent your own basis sets. You've all heard of triple zeta, how many of you have heard of 12 zeta (dodeca-zeta)? Anyway it's really ugly and even on a six-electron problem, you consume enormous amounts of computer time trying to do all this. Once you have the electron density, you say, what is the potential that causes this density in Walter's best sense. You find other numerical problems. For example, you can add a constant to any potential and wind up with the same density. You can add any function that wiggles faster than your basis set and wind up with the same density. Near the nucleus you can't tell because you have an infinite potential and you can't resolve the finite exchange correlation potential, that's the difference there. So when all these numerical difficulties come in, you keep saying, "Ahhh, how do I make this work?" And I drove one poor post doc to distraction

over a period of two years trying to make this numerical problem work out and we finally resolved it for this simple 6-electron model. Now the stuff you see in the literature is mostly atoms, the work of Umrigar and Gonze and others. The reason is very simple: atoms have spherical symmetry, there are all kinds of constraints that you can put on the potential that make it work out. As soon as you break spherical symmetry it gets harder. Now lithium diatomic has bilateral and axial symmetry and that helps a lot, too. But it's a nontrivial problem and as you get into more complex molecules I will tell anybody working here that to derive the exact potentials it is an extremely nasty numerical problem. But nevertheless we did so, and we tried to determine where the differences between gradient-corrected LDA and the exact potentials were coming from. And we noted an extremely important contribution; they were coming from lack of self-interaction correction, the biggest single correction to the potentials.

Now John Perdew and Alex Zunger, way back in 81, published what they considered a self-interaction correction in which basically you do the normal top two LDA terms, then you subtract off the electrostatic interaction of the charge with itself, and then the exchange correlation with that density as if it were the only density in the problem for each electron. Last year Lundin and Eriksson came up with a slight improvement which is the same first two terms, but in the exchange correlation you subtracted the density of each state from the density basically removing the interaction from that functional. The improvement is only a few percent, but it exists and it's right and it's no more difficult to do, so why not do it. The real difficulty with both these is that the potential that you get out varies from state to state so the answers are not Hermitian and that means that the states are not orthonormal that are the natural solutions for this. Now it turns out you can simply orthonormalize them and it doesn't make much difference. You can also say give me the minimum solution to the energy functional that gives orthonormal solutions or you can do linear combinations. John and Alex gave a density average potential as one possible way of handling this and it works reasonably well, but for a paper we gave in Spain, we worked out a simple thing that was related on a separable approximation and it worked quite well also. The biggest important thing in here is that you get more realistic potentials if you put these things in and you get better densities. You can compare the densities out with the exact densities and they work out better. One other thing that we discovered is that good energies don't mean good properties. And that's not too surprising when you think about it because, if you have an energy functional, if you add to it any functional that integrates to zero to it, you'll get the same energy, but the derivative properties of this may not be exactly the same and the derivative properties are what you want.

The largest single error in both the LDA and the GGA corrections to it are self-interaction and full self-interaction correction must be accomplished if DFT is to improve. I can't say that there's not other improvements, but my conclusions are the following: the good density functional theory must give good densities, who can argue with that? To test current density functional theories requires at least MP-4 (many-body perturbation theory) plus a fourth-order calculations with high precision basis sets. The potentials given by an improved DFT must more accurately reflect those potentials giving the exact densities. I don't care what the energy functional is. I want exact potentials

because they determine the densities and I can determine almost everything that I want in derivative properties without knowing the exact energy. So the biggest error again is the self-interaction.

And finally I'd like to make a point here what we call LCVT (linear combination of various theories) doesn't correct self-interaction unless full exchange is used. I'm not a big fan of hybrid theories, or 40 percent Lee Yang Parr and 22 percent LDA and various things. The reason people are in favor of that is because, for a large set of problems, it gives you the right energy, but energy doesn't give you anything else that you may want. So we need to correct the biggest errors of LDA. The self-interaction correction needs to be cast in such a way that it can be used in a Hermitian manner.

 These are one man's opinion based on a few years in the field. They're not to be treated as gospel, they certainly don't provide any answers to problems, but they are, I think, a place for a point of view that we do need to improve the theory. And you'll be hearing after the break from people who do believe that they have seen things that are wrong and things that need correcting. Now I've tried to finish about on time and make up for it so that we don't miss any of the break, but if you have any questions I'd be happy to answer them quickly. If not, you're missing your coffee.

Q: (Walter Kohn). At the beginning of your talk you said something, and that is these two facts that the LDA gives accuracies for not only the geometries of a minima of energy of the function of changing of positions of the atoms but also the curvatures; percentage-wise, usually, much better accuracies than for the total energy. Now if you haven't done the calculations, would you have guessed? Of course you can't expect such a high accuracy as for the total energy itself, just the opposite, and I think you pointed that out that that's a great puzzle. And then there is another puzzle that makes the energy much better by GGAs about an order of magnitude. We don't do those others. Two puzzles, are they connected, do you understand both or one?

MT: First I have to tell you a story about Professor Dirac, who was visiting the University of Texas when I was a grad student there many years ago. And he gave this long lecture at the board and a professor stood up and said, "Professor Dirac, I don't understand how you got from step 5 to step 6." Dirac stands there and says nothing and the moderator stands up and said, "Aren't you going to answer the question?" Professor Dirac said, "You didn't ask a question."

[Laughter]

It turns out if you start checking the energy errors of LDA and you start stripping electrons off an atom, you find out that the ionization potentials are not bad until you get to the 1s state and then the 1s state energies are really significantly in error, the 1s electron removal energies. But for most atoms, the total energy of the atom is bad, but the error is mostly in the 1s state as far as the things that I have done. The 1s states don't (a) enter very much into the chemistry if you're not dealing with hydrogen and (b) well

forget (b) so my feeling is that No. 1, the total energy errors, if you talk about ionization energies, are mostly in the 1s states. Secondly, and you're free to correct me….

WK: No, but I'm not talking about those total energies.

MT: Ok, but you say the energies are in error, why do we get good geometries?

WK: For example, cohesive energy, binding energy, it has nothing to do with the 1s electron.

MT: That's another issue. There is a systematic error in cohesive energies and binding energies, I agree with you. I would not expect to get good chemistry when the errors are as large as they do. That particular one I don't understand. I was only addressing the large total energy errors.

WK: The other one is the tough one.

MT: I agree with you, but my feeling is that we get essentially good correlated results because we're mimicking the results of the correlated calculation. That's a heuristic and I can't justify it any better than that. Why we don't get better geometry basically has been part of this talk, we don't get better potentials even if we get better numbers for total energies and it's the errors that we make in the distribution of the electron density that gives us the errors and the forces. Without good potentials, you can't get better ones even if you get a good number. So I believe I understand that one, Ok?

WK: Ok for you to believe it.

MT: Don't ask any more questions.

Q (John Perdew): My question is about salt sodium and we know that the LDA makes the lattice constant of salt sodium about 4 percent smaller than experiment?

MT: To tell you the truth, I don't know. I have restricted myself to the very lightest atoms that I can deal with because I can do the correlated calculations to check on them. Sodium is a little too heavy to do it easily, but we can find out.

JP: Not the atom, the salt.

MT: I know, I'm talking about what size atoms I'm willing to put into my calculation. But I can do an SIC calculation for sodium and tell you if it comes up with the right lattice constant unless you've already done so.

JP: No.

MT: That I can do, but I don't want to do the correlated calculation for it.

WK: Don't listen to him [Bill Goddard, who said something about self-interaction on one electron] because for an infinite system such as metallic sodium, which by the way is certainly in a pretty good approximation just a jellium model, the self-interaction for an infinite jellium model is included in the LDA.

MT: That's a good point. I think it gets the most serious when you have moderately localized orbitals like the electrons in some of the models. But nevertheless if you would like, we'll do a gradient-corrected LDA problem without the self-interaction correction and with it and tell you the results.

JP: I think the self-interaction here is one of the problems. I think you've identified one of the reasons why geometries and lattice constants are not more accurate. I think there is another problem, too, and that's associated with the core/valence interaction. I think the LDA and the GGA are doing very well for just the valence electrons, but they're not doing so well for the interaction that occurs when the valence electrons overlap with the cores in this very small region and there's some work by Martin Fuchs which seems to make the case for that very convincingly.

MT: We also saw that when we did our simple way to weighted density stuff, if we do core partitioning and separate out those two, that then the answers would get much better. So a simple model that ignores the difference certainly doesn't work out.

Kieron Burke: My question is very simple: what aspects of the potential need to be improved to give you better geometries and vibrations? Define a good potential in a sense.

MT: One that gives you a good density, how's that? The easiest feature to see is in an isolated molecule that clearly the minus 1 over r tail; the problem is that that's relatively unimportant to the density. What we see is basically, I think if we were to properly take and make our exchange models more energy dependent than, say LDA, is we would be better off. And I think we need to do that. If you'd look at the Hartree-Fock correction, if you'd have ˘   , if they are wildly different in energy, one's rapidly wiggling and the other one is not and they integrate rapidly to zero so you get very little interaction, if they're wiggling the same amount you can get fairly significant interactions so if the energies are very close they're significant, if they're not very close the cross terms go away and we need to take more account of that energy dependence to get a good potential. That's the one thing I can tell you and that's one of the problems with core densities versus valence densities, that all we have is the size of the density and we don't have any relative energy difference.

[Explanation to the speakers.]